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SPECIFICATION

INVENTION: METHOD AND DEVICE FOR CATALYTIC  
NITROGEN OXIDE REDUCTION OF MOTOR  
VEHICLE EXHAUST

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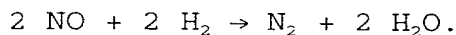
METHOD AND DEVICE FOR CATALYTIC NITROGEN OXIDE  
REDUCTION OF MOTOR VEHICLE EXHAUST

BACKGROUND AND SUMMARY OF THE INVENTION

The invention relates to a method and a device for catalytic  
5 reduction of nitrogen oxides for mobile applications and, more  
particularly, for reducing nitrogen oxides in the exhaust of  
motor vehicles by reduction on a catalyst with the addition of  
hydrogen. The hydrogen required for nitrogen oxide reduction is  
generated on-board the vehicle by water vapor reformation and/or  
10 by partial oxidation of hydrocarbons, for example, methanol,  
diesel fuel, or gasoline on a catalyst.

For the operation of motor vehicles with gasoline and,  
especially for diesel engines, the observation of the applicable  
legal emission guidelines is indispensable. In this connection,  
15 catalytic NO<sub>x</sub> reduction using hydrogen is being used  
advantageously.

This catalytic removal of nitrogen oxides from the  
combustion exhaust from motor vehicles is performed using  
hydrogen on suitable catalysts with the reaction



In the known method for removing nitrogen oxides by NO<sub>x</sub>  
reduction, the hydrogen required for the reaction is carried in  
the vehicle, for example in compressed gas tanks, liquid hydrogen  
tanks, or metal hydride storage devices. The disadvantage of  
25 this method is that large heavy containers are required to

transport the hydrogen. The cumbersome containers also have a narrowly limited capacity, hence requiring short intervals between refills.

European Patent document EP 0 537 968 A1 describes a device for catalytic reduction of nitrogen oxides in motor vehicle exhaust by addition of hydrogen. Hydrogen generation takes place aboard the motor vehicle by partial oxidation or reformation of methanol on a suitable catalyst. The heating of these catalysts is accomplished by placing them in the hot exhaust stream from the engine.

This device has the following disadvantages: 1) with the engine cold, for example shortly after starting, the catalyst is not yet active for reformation or partial oxidation; 2) the engine must be adjusted in such fashion that an excessive exhaust temperature is avoided throughout the entire lifetime of the engine, even briefly, in order to prevent irreversible deactivation of the catalyst; and 3) it has a relatively cumbersome size.

Hence, the object of the invention is to provide a method and a device to generate hydrogen in a motor vehicle which overcomes the disadvantages of the prior art described above.

These objects are achieved by the method for reducing nitrogen oxides in the exhaust of motor vehicles by reduction on a catalyst with the addition of hydrogen. The hydrogen required

for nitrogen oxide reduction is generated on-board the vehicle by water vapor reformation and/or by partial oxidation of hydrocarbons, for example, methanol, diesel fuel, or gasoline on a catalyst. The catalyst is adjustably heated for water vapor reformation or for partial oxidation. These objects are further achieved by the device for reduction of nitrogen oxides in the exhaust of motor vehicles by catalytic reduction, including a reactor containing a catalyst on which the nitrogen oxide reduction is performed by the addition of hydrogen; a device for generating hydrogen located on-board the motor vehicle and including a reactor for water vapor reformation of hydrocarbons on a catalyst and/or a reactor for partial oxidation of hydrocarbons on a catalyst. An adjustable heating device is provided for the reactor for water vapor reformation and for the reactor for partial oxidation.

According to the present invention, the catalyst used to generate the hydrogen is adjustably heated for reformation of hydrocarbons.

The device according to the present invention includes an adjustable, especially an electrical, heating device by which, independently of the hot engine exhaust, the catalyst can be brought to a predetermined temperature and kept there.

The adjustable heating of the catalyst according to the invention for reformation of hydrocarbons has the following advantages: 1) by preheating the catalyst, its activation can

occur as soon as the engine starts; 2) it is possible to keep the catalyst operationally ready (standby operation) even when the vehicle is parked for some time; 3) the catalyst can be operated at its optimum operating temperature through temperature regulation; 4) in contrast to known devices which heat the catalyst using hot engine exhaust, the temperature can be regulated flexibly and independently of the operating state of the engine, and damage to the catalyst (deactivation) is always avoided; and 5) in contrast to known devices, the result is a compact unit with small dimensions which can easily be integrated as a separate module into an existing device, for example through the use of a flange.

Other objects, advantages and novel features of the present invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic block diagram illustrating the process of water vapor reformation from methanol;

Figure 2 illustrates a reactor for performing water vapor reformation from methanol;

Figure 3 is a schematic block diagram illustrating the process of partial oxidation of methanol;

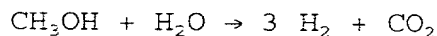
Figure 4 illustrates a reactor for performing partial oxidation of methanol; and

Figures 5a and 5b illustrate another reactor for performing partial oxidation or for water vapor reformation.

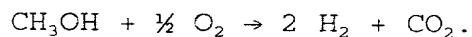
## 5 DETAILED DESCRIPTION OF THE DRAWINGS

H<sub>2</sub> generation for NO reduction takes place aboard the motor vehicle by reformation of hydrocarbons. Methanol is especially suitable for this purpose. Diesel fuel or gasoline may also be used for reformation.

One advantageous reaction in this regard is the water vapor reformation from methanol by the equation



and partial oxidation of methanol by the equation



The first reaction is endothermal and can be performed with catalysts that are known of themselves, for example catalysts with the active components copper and zinc, at only 200 to 400°C.

The second reaction is exothermal and is likewise performed with the support of catalysts that are known of themselves, for example Pt, Pd, Ru, or CuZnO.

In both reactions, depending on the operation of the reactors, CO is produced in a range from several hundred ppm to several percent.

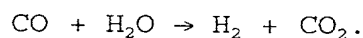
The processes of water vapor reformation and partial oxidation of other hydrocarbons are known and proceed in accordance with comparable equations but under different reaction conditions (mainly, higher temperatures) and possibly with other catalysts. However, for the process performance and reactor variations the same remarks apply in theory as described below for the special case of methanol.

In one advantageous embodiment, hydrogen generation can also be performed by a mixed reaction composed of water vapor reformation and partial oxidation.

#### Water Vapor Reformation from Methanol (Figures 1 and 2)

Figure 1 shows the process of water vapor reformation from methanol. Initially, a water-methanol mixture is delivered from a tank, preferably with a molar ratio of methanol to water of 1:1 to 1:2. The tank can be under ambient pressure. Delivery is by means of a pump that assumes the metering function directly as a function of the load through a suitable control (rpm regulation, for example). Alternatively, the liquids can be delivered through a constantly operating pump, with subsequent metering being performed for example by solenoid valves, operating comparably to the injection valves in a motor vehicle. Then, the water-methanol mixture is evaporated in an evaporator

and fed to the reactor. In the reactor, with the addition of heat to the catalyst, the conversion into hydrogen and CO<sub>2</sub> and H<sub>2</sub> takes place. According to the invention, direct heating of the catalyst is provided. Preferably, an electrical resistance heater can be used here as a heat source. The addition of heat to the reactor can be adjusted, for example, by a temperature regulator in the catalyst. Possibly the CO component of the gas product can then be lowered in another reaction stage and/or the hydrogen yield can be increased, for example, by means of the known shift reaction:



Instead of water and methanol being stored as a mixture in the same tank, the water and methanol can be stored separately from one another in different tanks and delivered from them.

Figure 2 shows one advantageous embodiment of a reactor for performing the water vapor reformation of hydrocarbons. It is in the form of a tube 10, preferably with an inside diameter of 5 to 50 mm. The reactor is divided into three stages 12, 14 and 16. In the center 14 is the main reaction stage in which a catalyst 18 is located. This is where the water vapor reformation takes place. The catalyst 18 is present in the form of loose material but monolithic materials can be used as well. An evaporator section 12 is located upstream from the main reaction stage 14, in which the water-methanol mixture is evaporated as it enters. An aftertreatment stage 16 is located



downstream from the main reaction stage 14. This is where the CO that is produced is reduced by means of a shift reaction.

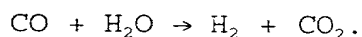
The figure also shows an electrical heater 20 according to the invention by which the catalyst in the main reaction zone is heated. In this case, the electrical heater is located in the reaction chamber itself but can also be located in the outer area of the tube. In addition, the heating of the reactor can also be performed by the hot exhaust from the internal combustion engine of the motor vehicle. In this case, the hot exhaust stream is guided over ribs (22, shown in dotted lines) provided on the outside wall of the reactor.

The figure also shows that the evaporator stage 12 is also heated by the above-mentioned heating arrangement 20. However, embodiments are also possible in which the individual stages including the aftertreatment stage 16 can be heated independently of one another. Thus the evaporator stage 2 in particular can be heated more strongly than the reformer stage (main reaction stage) 14. The aftertreatment stage 16 is heated only slightly, if at all, so that the corresponding heating is not shown here.

#### Partial Oxidation of Methanol (Figures 3 and 4)

Figure 3 shows the process of partial oxidation of methanol. Initially, a water-methanol mixture is supplied from a tank, preferably with a molar ratio of methanol to water of 1:0 to 1:2. The tank in this case can be at ambient pressure. Delivery is by means of a pump which may assume the metering function

directly as a function of load through the use of a suitable control, for example, rpm regulation. Alternatively, the liquids can be delivered through a constantly operating pump, with subsequent metering being performed for example by solenoid valves comparable to the injection valves in a motor vehicle. Then, the water-methanol mixture is evaporated, air is fed to the vapor mixture through a compressor, for example a diaphragm pump, and the mixture is admitted to the reactor. In the reactor the exothermal conversion to hydrogen and CO<sub>2</sub> and H<sub>2</sub> takes place on a catalyst. Advantageously, the CO component of the gas product can then be reduced in a subsequent reactor stage and/or the hydrogen yield can be increased, for example by means of the known shift reaction:



As in the process described above for water vapor reformation, water and methanol can be used instead, stored as a mixture in the same tank, or they can be stored separately from one another in different tanks and be delivered from them. The water can also be supplied advantageously only after partial oxidation. This has the advantage that the CO content is additionally reduced.

Figure 4 shows a concrete embodiment of a reactor for performing partial oxidation of methanol. It is in the form of a tube 30 whose inside diameter is preferably 5 to 50 mm.

Once again the main reaction stage 32 is located in the center, together with the catalyst 34 on which partial oxidation takes place. According to the invention, adjustable heating is provided for the catalyst in the form of an electrical resistance heater 36.

In the tubular reactor, connected upstream from the main reaction stage 32, an evaporator stage 38 is located that is heated by an electrical heater 40. Instead of or in addition to this heating, a feed device can be provided with which the hot product gases that are produced during partial oxidation on the catalyst can be supplied for example in a countercurrent on the outside wall of the reactor.

Between the evaporator stage 38 and the main reaction stage 32 is a mixing stage 42 in which the methanol-water mixture in vapor form is mixed with air admitted from the outside and conducted into the reforming stage 32. The reforming stage is followed by a gas aftertreatment stage 44 in which further reaction of the remaining methanol with water vapor takes place and/or the resultant CO is reduced with water vapor in a shift reaction. This stage is heated only slightly, if at all, so that the corresponding heating is not shown here.

Figures 5a and 5b show another reactor whose theoretical design can be used both for water vapor reformation and for partial oxidation of hydrocarbons. Figure 5a shows a section through the reactor in the radial direction. Figure 5b shows a

section in the axial direction along line AB in Figure 5a. Sample dimensions are given (in mm). The reactor consists of a compact cylindrical body including a plurality of axial holes. Four of these axial holes contain the catalyst, as loose material for example. The four additional axial holes, which in this embodiment have a smaller diameter by comparison with the holes for the catalyst, constitute the evaporator stage. Another hole is provided in the center of the reactor. This center hole contains a heating cartridge. Since this heating cartridge is surrounded by both the evaporator holes and the catalyst holes, it can be used both for evaporation and for heating the catalyst according to the present invention. Optionally, the outer jacket of the reactor can be provided with thermal insulation in order to keep heat loss as low as possible. Reformation of methanol then takes place in such fashion that the methanol/oxygen mixture is conducted into the holes in the evaporator and then is conducted in the opposite direction through the holes that are filled with catalyst.

Although the invention has been described and illustrated in detail, it is to be clearly understood that the same is by way of illustration and example, and is not to be taken by way of limitation. The spirit and scope of the present invention are to be limited only by the terms of the appended claims.